

HYDROGEOCHEMICAL CHARACTERIZATION AND GROUNDWATER QUALITY OF THE DONG GIAO KARST AQUIFER IN TAM DIEP, NINH BINH, VIETNAM

HIDROGEOKEMIČNA KARAKTERIZACIJA IN KAKOVOST PODZEMNE VODE KRAŠKEGA VODONOSNIKA DONG GIAO V TAM DIEP, NINH BINH, VIETNAM

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Abstract

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Vu Thi Minh Nguyet, Vu Phuong Thanh, Vu Dinh Hai, Nguyen Duc Roi & Doan Thi Thu Tra: Hydrogeochemical characterization and groundwater quality of the Dong Giao Karst aquifer in Tam Diep, Ninh Binh, Vietnam

The Dong Giao karst aquifer is a major source of drinking water for domestic and agriculture use in Tam Diep city. Understanding of hydrogeochemical characteristics and water quality of the karst aquifer are useful information for sustainable use and protection of groundwater in the area. A total of 30 water samples from the main karst springs and domestic wells were collected to identify the physical property, chemical composition of karst water and water-rock interaction. Physico-chemical parameters (pH, water temperature, electrical conductivity and alkalinity) and major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , NO_3^- , Cl^-) were measured *in situ* and analyzed in the lab. Water samples from drinking water source Spring 18 and other important karst springs were taken to detect *Escherichia coli* (*E.coli*). A tracer test was also carried out for providing contamination information. Results show that the hydrochemical types of Tam Diep groundwater were of calcium magnesium bicarbonate (Ca-Mg-HCO_3) and calcium bicarbonate (Ca-HCO_3). The carbonate dissolution line and Ca/Mg ratios clearly indicated that the weathering of carbonate rocks (limestone and dolomite) is the dominant process controlling the chemistry of groundwater of the test site. Chemical quality of groundwater ranks from good to excellent for drinking and irrigation, and total hardness values are relatively high. In contrast, all microbial samples contain high number of *E.coli* and thus by microbial standards, spring water quality is unsafe for drinking. This bacterial contamination mainly results from untreated domestic wastewaters, city sewage, and human activities in the Tam Diep area.

Key words: karst hydrogeochemistry, karst water quality, drinking water protection, Tam Diep, Vietnam.

Izveček

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Vu Thi Minh Nguyet, Vu Phuong Thanh, Vu Dinh Hai, Nguyen Duc Roi & Doan Thi Thu Tra: Hidrogeokemična karakterizacija in kakovost podzemne vode kraškega vodonosnika Dong Giao v Tam Diep, Ninh Binh, Vietnam

Kraški vodonosnik Dong Giao je poglavitni vir pitne vode za gospodinjstva in kmetijstvo v mestu Tam Diep. Razumevanje hidrogeokemičnih lastnosti in kakovosti vode kraškega vodonosnika so koristne informacije za trajnostno rabo in varovanje podzemne vode na tem območju. Skupno je bilo vzetih 30 vzorcev vode iz večjih kraških izvirov in vodnjakov za prepoznavanje fizičnih lastnosti in kemične sestave kraške vode ter interakcije vode in kamnine. Fizikalno-kemični parametri (pH, temperatura vode, električna prevodnost in alkalnost) in glavni ioni (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , NO_3^- , Cl^-) so bili merjeni *in situ* in analizirani v laboratoriju. Vzorci vode iz vira pitne vode Izvir 18 in drugih pomembnih kraških izvirov so bili preizkušeni na vsebnost *Escherichia coli* (*E. coli*). Izveden je bil tudi sledilni poskus, da bi pridobili informacije o onesaženju. Rezultati kažejo, da spadajo podzemne vode vodonosnika Tam Diep v kalcijev-magnezijev-bikarbonatni (Ca-Mg-HCO_3) hidrogeokemični tip in kalcijev-bikarbonatni (Ca-HCO_3) hidrogeokemični tip. Meja raztapljanja karbonatov in razmerje Ca/Mg sta jasno pokazali, da je preperevanje karbonatnih kamnin (apnenca in dolomita) prevladujoči proces, ki pogojuje kemične lastnosti podzemne vode na testnem območju. Kemijska kakovost podzemne vode se uvršča med dobro in odlično za pitje in namakanje. Celokupna trdota vode je razmeroma visoka. Nasprotno, vsi mikrobiološki vzorci vsebujejo veliko število *E. coli*, torej z vidika mikrobioloških standardov kakovost izvirske vode ne ustreza vrednostim za pitno vodo. Ta bakterijska kontaminacija v glavnem izhaja iz neočiščenih gospodinjstskih odpadnih voda, mestne kanalizacije in drugih človekovih dejavnosti v območju Tam Diep.

Ključne besede: kraška hidrogeokemija, kakovost kraške vode, varovanje pitne vode, Tam Diep, Vietnam.

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INTRODUCTION

Karst covers about 18 % of the land surface of northern Vietnam and plays an important role for socio-economic development of the country. Karst waters are major sources of water supply for domestic, industrial and agricultural sectors in many towns, villages and rural areas of Vietnam. However, karst springs and groundwater sources are under pressure in response to urbanization, economic development and population growth. Karst aquifers are particularly vulnerable to contamination resulting from human activities (Zwalen *et al.* 2004; Ford & Williams 2007; Goldscheider 2012). Karst groundwater consequently requires special consideration and protection. The sustainable management and protection of karst water resource is necessary and challenges the future development of the countryside in karst areas.

Hydrochemical investigation provides significant information about water quality, characteristics of karst system (Hunkeler & Mudry 2007; Mudarra & Andreo 2010; Barberá & Andreo 2012) and also a scientific basis for the development of sustainable management and protection plans (Nguyet & Goldscheider 2006; Hunkeler & Mudry 2007; Sánchez *et al.* 2015). The hydrochemical techniques have been widely applied in karst aquifers around the world. To understand the geochemical processes and characterize karst aquifers, geochemical models based on thermodynamic assumptions are used (Ford & Williams 2007; Parkhurst & Appelo 2011).

The hydrogeochemical methods have been applied in karst aquifers in Vietnam mainly for assessment of water quality and presentation of hydrogeochemical

parameters in comparison with Vietnamese standards (MONRE 2008). On the other hand, field observation and interpretation were conducted similar to those for porous and fissured aquifers on most of the groundwater system. The understanding of geochemistry of karst waters, carbonate dissolution as well as water-rock interaction is still limited. The application of tracing technique in karst hydrogeology research is scarce and should be considered more often. Hence, it is necessary to enhance hydrogeological and hydrogeochemical investigations and the application of tracing techniques in carbonate aquifers in Vietnam to provide information on karst processes and to protect karst water resources.

Tam Diep is a mountainous city located in the southwest of Ninh Binh province. The city is a gateway connecting the Red River Delta and the North Central Coast of Vietnam. In 2005, the city had an estimated population of 50,000 inhabitants and in 2015 expanded to 104,000 inhabitants. This area has typical karst landscape characterized by tower karst, karst field, sinkholes and karst springs. Karst water is the major water source for drinking, agriculture and industrial activities in the area.

This study aims to present the hydrochemical characterization and to determine the factors that govern the composition of karst water in the Tam Diep area. The assessment of chemical and microbiological groundwater quality are evaluated. This work is also the first attempt to investigate karst groundwater flow paths and contamination sources in the area by using tracing techniques.

STUDY AREA

GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

The Tam Diep area is located at the end of an extensive carbonate belt, about 90 km south of Hanoi. The area mostly consists of Triassic sedimentary rocks of the Tan Lac, Dong Giao and Nam Tham Formations, while Neogene sedimentary rocks of Hang Mon Formation and Quaternary deposits partially cover the center of the area (Fig. 1). The Early Triassic Tan Lac Formation is 500–540 m thick and predominately consists of marls. The most dominant rocks are the 800–1000 m thick carbonates of the Middle Triassic, Dong Giao Formation. The siltstone, sand and clay of the Middle Triassic Nam Tham Formation form the southwestern part of the area. Conglomerates of the Neogene Hang Mon Formation

and Quaternary gravel, clay and silt deposits thinly cover the center of the area. Structurally, the area is characterized by a number of folds oriented in a NW–SE direction. The carbonate rocks of Dong Giao Formation are folded along the axis with wavelengths of about 1–4 km and amplitudes of 0.3–0.8 km. Small folds with short axis and wavelengths are observed in non-carbonate rocks of Tan Lac and Nam Tham formations (Thin *et al.* 1982). Within the investigated area, the faults are dominated by NW–SE trends and noted as F1, F2, F3 and F4 (Fig. 1). Several short and discontinuous faults in the NE–SW direction are also observed at the site.

Hydrogeologically, the area is characterized by a thick karst aquifer of the Dong Giao Formation, which consists of limestone, dolomitic limestone and dolo-

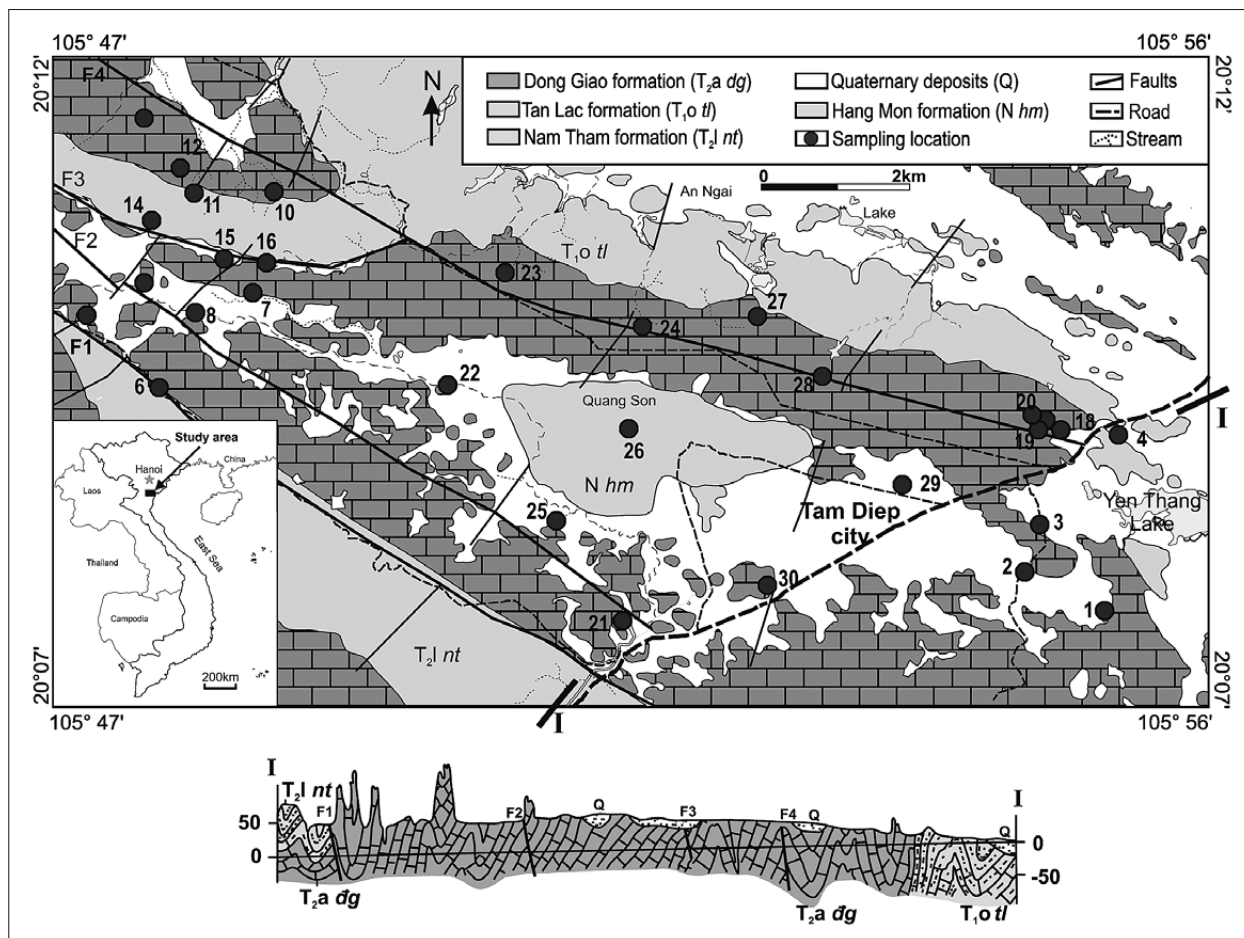


Fig. 1: Geological sketch of the Tam Diep area and groundwater sampling locations.

mite. The springs occurring within this aquifer are major source for drinking water and irrigation. For instance, the Suoi Genh spring (named spring 18) is used as an important drinking water source for Tam Diep city. This spring has estimated discharge ranging from 250 to 500 L/s. A number of water wells are used at the Dong Giao farms, as additional water sources for the area. The karst aquifer is recharged directly by rainwater where the carbonate rocks outcrop, or by water infiltration from low permeable rocks of the Nam Tham and Hang Mon formations. Intermittent surface runoffs occur along quaternary deposits, which are also discharging into the karst aquifer. The aquifer discharge through springs situated along the faults or at the interface between the permeable carbonate rocks and the impervious rock of the Tan Lac Formation.

LAND USE ACTIVITIES

Land use activities in the Tam Diep area include city and villages, cropping activities, livestock activities, several carbonate quarries and forest land. The urbanized area is situated at SE part of the region along both sides of the National Road (Fig. 1), while the villages are scattered throughout the region. Cropping activities of the Dong Giao farm including pineapples, and sugarcane are important and well known land uses in the Tam Diep area. This farm is located at the center of the region and occupies about 35 % of the area. There are also rice paddies, and peanuts and cassavas are grown in the nearby villages. Livestock activities mainly include several pig breeding farms in the center of the region and the grazing of goats in the highland area. Several small to medium carbonate quarries are still exploited in the region. Various land use activities in the Tam Diep area thus are potential contamination sources into karst aquifer as well as to the environment in the area.

METHODS

GROUNDWATER SAMPLING AND ANALYSES

Field measurements and hydrogeochemical samples were taken in October 2015 from 30 representative karst springs and wells used for domestic and irrigation purposes in the Tam Diep city. Locations of sampling sites are shown in Fig. 1. Physical parameters including pH, temperature and electrical conductivity (SpC) were measured *in situ* using a pH/EC 340i WTW Meter. For the first time at this site an Aqua Merck Alkalinity Test was used to titrate the water samples *in situ*. All water samples were filtered using a 0.45 μm Millipore and collected in 350 mL plastic bottles. Cation samples were treated with HCl 3M to a pH of 2.

Chemical analyses were done at the Institute of Chemistry, Vietnam Academy of Science and Technology, following the Standard Methods for the Examination of Water and Wastewater. Major cation concentrations (Ca^{2+} , Mg^{2+}) were analyzed by the EDTA titrimetric method, while concentrations of K^+ and Na^+ were determined by using Flame Photometric and Flame Emission Photometric method respectively. To determine the concentrations of Cl^- and SO_4^{2-} anions, the Silver nitrate titration and turbidimetric methods were applied. The concentrations of NH_4^+ and NO_3^- were determined by using the APHA 4500 method. Estimated accuracy of the analysis results by electrical balance was within $\pm 5\%$.

The microbiological samples were taken at drinking water spring 18 and seven other karst springs in 2012. Samples were collected in sterilized bottles of 50 mL and placed on ice in a cooler for transport. Within 24 hours, the collected samples were analyzed for *Escherichia coli* (*E.coli*) by multiple tube (most probable number) method at the School of Environmental Science and Technology – Hanoi University of Science and Technology.

TRACING EXPERIMENT

A preliminary tracing experiment was carried out in the Tam Diep area in October 2012. The goal of this test was to determine the existence of underground water flow path(s) between karst springs; and to provide information of contamination transport in spring 18 (Suoi Genh spring), which is used as a drinking water supply station for Tam Diep city (Fig. 2). Field observations assume that this spring could be connected to the spring 20, located about 280 m to the NW. To avoid color contamination on drinking water springs, only 20 g of dry powder uranine were dissolved and injected at spring 20. A field fluorometer GGUN-FL30 was installed at spring 18 for continuous monitoring uranine concentration and charcoal bags were installed at two other springs (17 and 19) for 7 days.



Fig. 2: Drinking water spring 18 (Suoi Genh spring) and pump station (Photo: V. T. M. Nguyet).

RESULTS AND DISCUSSION

HYDROCHEMICAL CHARACTERISTICS AND WATER-ROCK INTERACTIONS

Physical properties of groundwater

Tab. 1 gives the general characteristic of groundwater samples in the Tam Diep area. All karst groundwater is neutral with pH ranging from 6.45 to 7.7, while temperature ranges from 24.8 °C to 28.7 °C. The electrical conductivity (SpC) values range from 285 $\mu\text{S}/\text{cm}$ to 725 $\mu\text{S}/\text{cm}$ with an average value of 454.6 $\mu\text{S}/\text{cm}$. Several groundwater samples (spring No. 10, 11 and 14 in Fig. 1) collected

near the contact with non-carbonate terrain are characterized by relatively lower electrical conductivity values ranging from 175 $\mu\text{S}/\text{cm}$ to 318 $\mu\text{S}/\text{cm}$. The high variations of electrical conductivity values measured in this karst aquifer show the possible influence of weathering processes of the host rock and local geological settings.

Chemical characteristic

The Ca^{2+} and Mg^{2+} are the dominant cations in groundwater in the area. The concentrations of Ca^{2+} and Mg^{2+}

Tab. 1: Physico-chemical parameters and major ions concentrations of Tam Diep groundwater.

Parameters	Min	Max	Mean	WHO guideline values (2011)	Vietnamese guideline (09:2008/MONRE)	Sample exceeding guideline value
Temp (°C)	24.8	28.7	26.06			
pH	6.45	7.7	7.07	6.5–8.5	5.5 – 8.5	None
SpC (µS/cm)	175	725	423.2	1500	1500	None
Ca ²⁺ (mg/L)	22.4	96.8	62	75		2,4,5,7,14,19
Mg ²⁺ (mg/L)	2.88	35.04	12.15	50		None
Na ⁺ (mg/L)	1.103	17.52	4.96	200		None
K ⁺ (mg/L)	0.004	1.156	0.19	12		None
HCO ₃ ⁻ (mg/L)	94.58	384.42	234.62	500		None
SO ₄ ²⁻ (mg/L)	2.11	27.97	6.36	250	400	None
Cl ⁻ (mg/L)	7.4	31.6	14.37	250	250	None
NO ₃ ⁻ (mg/L)	0.26	13.27	5.61	50	15	None
TH (mg/L)	83.74	355.08	204.86		500	None

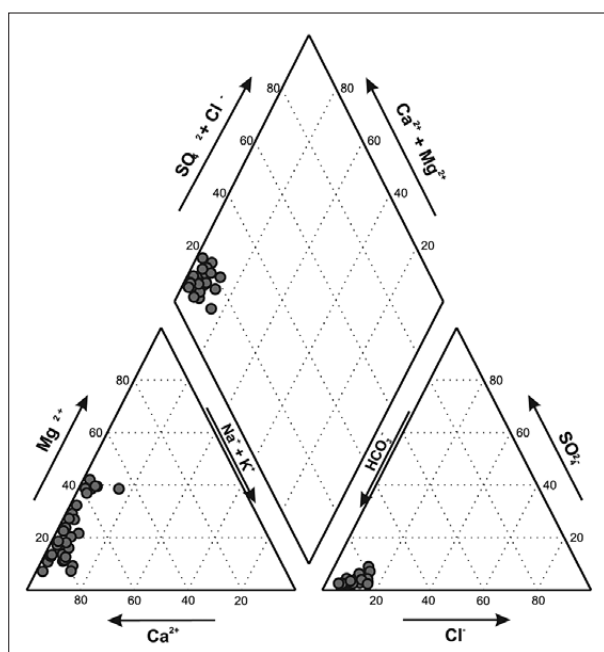


Fig. 3: Piper diagram of groundwater samples in the Tam Diep area.

range from 22.4 mg/L to 96.8 mg/L and from 2.88 mg/L to 35.04 mg/L respectively, with mean concentration of 62 mg/L and 12.15 mg/L (Tab. 1). A relatively lower concentration of Ca²⁺ and Mg²⁺ is detected in some samples collected near the contact between karst and non-karst terrain. All groundwater samples have low concentration of Na⁺ and K⁺, below 17.52 mg/L and 1.156 mg/L respectively.

The concentrations of HCO₃⁻ range from 94.58 mg/L to 384.42 mg/L with mean concentration of 234.42 mg/L in this aquifer. However, considerably low HCO₃⁻ values (< 135 mg/L) are determined in the groundwater sam-

ples collected in the vicinity of non-karst rocks. The SO₄²⁻ values are highly variability in groundwater samples, ranging from 2.11 to 27.97 mg/L. The concentrations of Cl⁻ range from 7.4 mg/L to 31.1 mg/L and NO₃⁻ from 0.26mg/L to 13.27 mg/L.

The Piper diagram shows hydrochemical facies of groundwater in the area (Fig. 3). The hydrochemical types of Tam Diep groundwater were of calcium magnesium bicarbonate Ca-Mg-HCO₃ type and calcium bicarbonate Ca-HCO₃ type. The hydrochemical facies suggest that dissolution processes of the carbonate rocks of the Dong Giao Formation control the hydrochemistry of groundwater. The calcium bicarbonate water resulted mainly from dissolution of limestones and calcium-magnesium bicarbonate resulted from dissolution of dolostone in the catchment area.

Water-rock interaction

The Gibb (1970) diagram is the most useful tool to identify the mechanism controlling natural water chemistry. A semi logarithmic plot of total dissolved solids (TDS) versus weight ratio of cations Na/Na+Ca or weight ratio of anions Cl/Cl+HCO₃ provides information on the mechanisms controlling the chemistry of water such as atmospheric precipitation, rock dominant and evaporation-crystallization processes. Gibb's methods have recently been applied in a number of groundwater studies of carbonate aquifers to identify hydrochemistry origins (Krishna Kumar *et al.* 2012; Pu *et al.* 2015). Applying Gibb method for groundwater in the Tam Diep area indicates that hydrochemistry composition of groundwater in the area is controlled by rock dominant processes. The relation of total calcium and magnesium to alkalinity (in Fig. 4) shows that groundwater samples are well fitted to dissolution line 1:2, indicating the weathering of carbonates within the aquifer in the area.

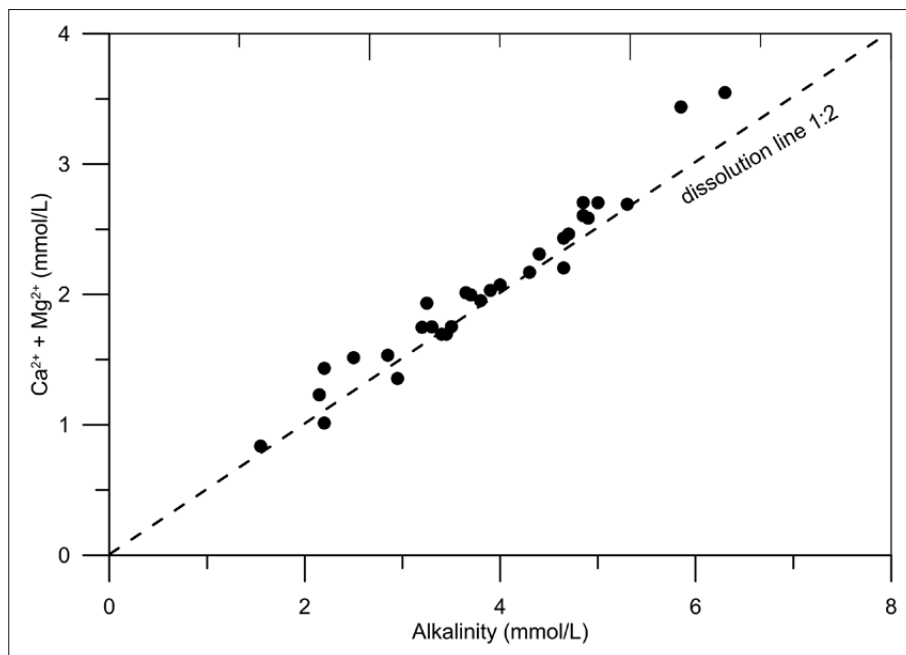


Fig. 4: Calcium and magnesium versus alkalinity in Tam Diep groundwater.

Moreover, the molar ration of Mg/Ca (Fig. 5) in the collected groundwater samples provides further information on water-rock interaction in the area. The Mg/Ca is a useful parameter providing the lithological composition of carbonate rock through which the water sample circulated (White 1988). A ratio Mg/Ca = 1 is for dissolved water from dolomite; in contrast, a ratio Mg/Ca = 0 is for dissolved water from pure calcite. A ratio Mg/Ca of 0.5 indicates the equilibrium of water with both calcite and dolomite. Most of the groundwa-

ter samples are below the line of 0.5 (Fig. 3), suggesting dominant calcite in carbonate rocks of the area. The plot also shows that some samples above the line of 0.5 are influenced by dissolution of dolomitic limestone or dolomite in the bedrock of the area. This evidence confirms the presence of limestone and dolomite in the carbonate rocks of Dong Giao Formation, which was noted by Thinh *et al.* (1982), and Huu and Huong (2012).

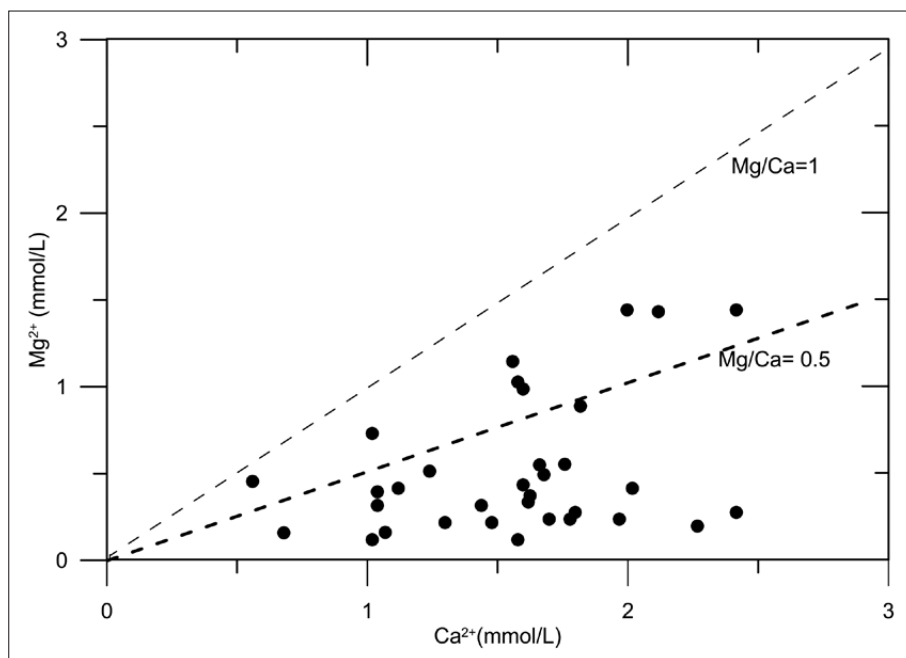


Fig. 5: Molar ratio of magnesium to calcium in Tam Diep groundwater.

KARST WATER QUALITY

Drinking water quality

The concentration of major ions in the groundwater samples and their comparison with the World Health Organization (WHO) and Vietnamese drinking water standards are given in Tab. 1. In general, the concentration of major ions of groundwater samples are within acceptable limits of both WHO and Vietnamese standards. However, a small number of samples (6 of 30 samples) show calcium concentration higher than 75 mg/L. A useful water quality parameter: total hardness, which measures combined concentrations of Ca^{2+} and Mg^{2+} in the water, is also considered in this study. Total hardness (as mg/L CaCO_3) of groundwater samples was calculated by using the following equation (White 2010):

$$\text{TH} = 100.09 \left(\frac{\text{Ca (mg/L)}}{40.08} + \frac{\text{Mg (mg/L)}}{24.305} \right)$$

Based on total hardness values, four types of water are classified: < 75 mg/L CaCO_3 as soft; 75–150 mg/L CaCO_3 as moderately hard; 150–300 mg/L CaCO_3 as hard; and >300 mg/L CaCO_3 as very hard (US–EPA 1986). Both extreme degrees of very soft (<75 mg/L as CaCO_3) and very hard (>300 mg/L as CaCO_3) are considered as undesirable features in water. Waters with hardness in excess of 500 mg/L are not suitable for most domestic purposes. The total hardness values of Tam Diep groundwater are shown in Tab. 1. All samples have hardness values below allowable limit for domestic uses; however, most of the groundwater samples (24 of 30 samples) fall into hard to very hard category. The elevated total hardness values in Tam Diep groundwater samples indicated the high amount of Dong Giao carbonate rock taken into solution.

Irrigation water quality

Sodium absorption ration (SAR) is commonly used as an index to determine groundwater quality for irrigation. SAR is an important parameter to measure the sodium hazard for groundwater having high bicarbonate concentrations. Therefore, water quality of the collected groundwater samples was evaluated by determining SAR. The SAR was defined by the following equation (Wilcox 1955):

$$\text{SAR} = \frac{\text{Na}}{\sqrt{(\text{Ca} + \text{Mg})/2}}$$

where, concentrations are expressed in meq/L

Water having high SAR values is not suitable for irrigation because it can damage the soil structure and create permeability problem. If the SAR value < 10, the water is safe for irrigation. The SAR values of Tam Diep groundwater samples are all less than 0.2, which indicates excellent quality for irrigation purpose.

Correlation between electrical conductivity, hardness and bicarbonate

Ca^{2+} , Mg^{2+} and HCO_3^- are major ions which are involved in geochemical reactions in karst and chemical classification of groundwater in Tam Diep area. In these instances when chemical analyses are not available during the sampling period, field measurements will be used. A correlation between SpC values that is easily measured *in situ* with dominant chemical ions will be useful for further hydrogeochemical studies and for monitoring of water quality in the area. The relationship between hardness, bicarbonate and SpC, therefore, was established based on the collected water samples (n=30) in the Tam Diep area. The following equations are presented as follows:

$$\begin{aligned} \text{Hardness (mg/L as CaCO}_3) &= 0.4431 \text{ SpC} + 17.339 & R^2 &= 0.92 \\ \text{HCO}_3^- \text{ (mg/L)} &= 0.4763 \text{ SpC} + 33.058 & R^2 &= 0.879 \end{aligned}$$

where SpC is the electrical conductivity of water in $\mu\text{S/cm}$.

Groundwater flow path and bacterial contamination

Groundwater flow path

The uranine dye was injected into spring 20. A tracer breakthrough curve of dye tracer uranine was observed at the spring 18 (Fig. 6). The uranine tracer was first detected at spring 18 after only 120 minutes, while the maximum uranine concentration (5.56 $\mu\text{g/L}$) was attained 156 minutes after injection. After 400 minutes the concentration was below the detection limit. With a distance of 250 m between the injection point and sampling point, the calculated maximum tracer velocity is approximately 125 m/h and dominant tracer velocity is 59 m/h. Although tracer recovery rate was not calculated due to lack of data of flow measurement or discharge estimation, this experiment has proved an existence of an underground flow path between spring 20 and spring 18. The results obtained in this experiment thus provide useful information of contamination transport to spring 18 which is an important source supplying drinking water for Tam Diep city.

Bacterial contamination

Water samples taken at the most important karst springs in August 2012 were analyzed for *Escherichia coli* (*E.coli*) by multiple tube (most probable number) method. The result shows that all collected samples contained *Escherichia coli* with values ranging from 21 to 1100 (MPN/100 mL). The presence of *E.coli* is highly variable and exceeds the limit for drinking water, which state that coliform bacteria must be absent in a 100 mL water. The *E.coli* content at karst springs in the developed urban area (spring 17, 18 and 19) seems much

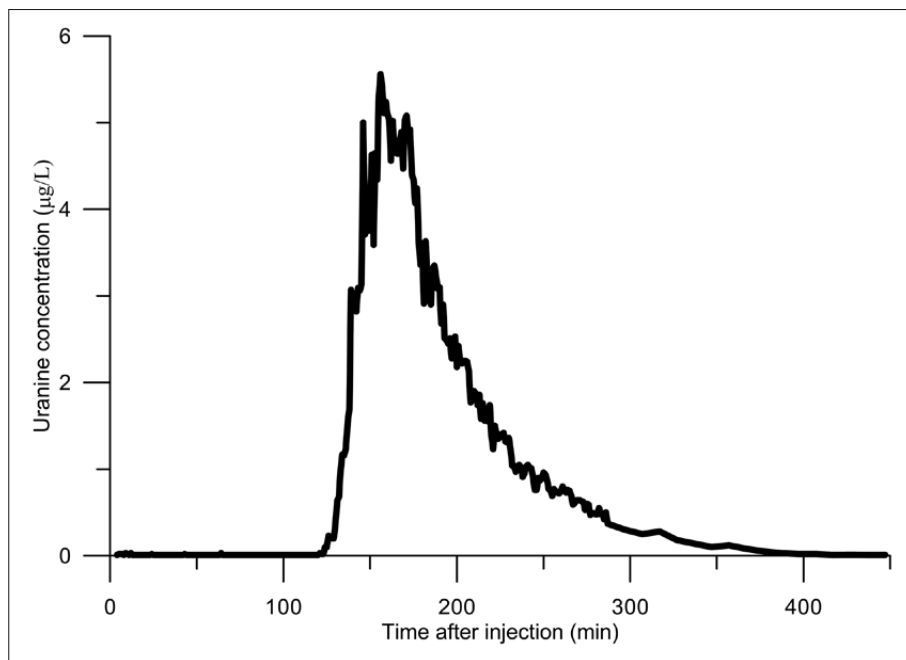


Fig. 6: Uranine tracer breakthrough curve recorded at spring 18 in October 2012.

higher than that at springs in other location. Moreover, all samples regularly taken at the drinking water spring 18 from August 2102 to December 2012 also detected *E.coli* (Fig. 7). The counts of *Escherichia coli* were highly variable and exceeded 93 MPN/100 mL in all samples of this drinking water spring. Moreover, samples collected during storm events in September and October 2012 show extremely high *E.coli* content, maximum to 110,000 MPN/100 mL.

Because of their hydrogeological characterization, karst aquifers are vulnerable to microbial contamination (Pronk *et al.* 2006; Nguyet & Goldscheider 2006). In-

creased urbanization, intensification of agriculture and human activities are impacts to bacterial water quality of karst groundwater (Pasquarell & Boyer 1995; Drew & Hötzl 1999). The bacterial contamination in Tam Diep karst water could be due to untreated domestic waste water, scattered waste and sewage disposal as well as cropping and livestock activities. The higher numbers of fecal coliforms in springs in urban zone compared to other locations may be due to increased anthropogenic activities, city sewage and the higher population density. Daily water to body contact (bathing, washing...) directly at karst springs, including spring 18, may also

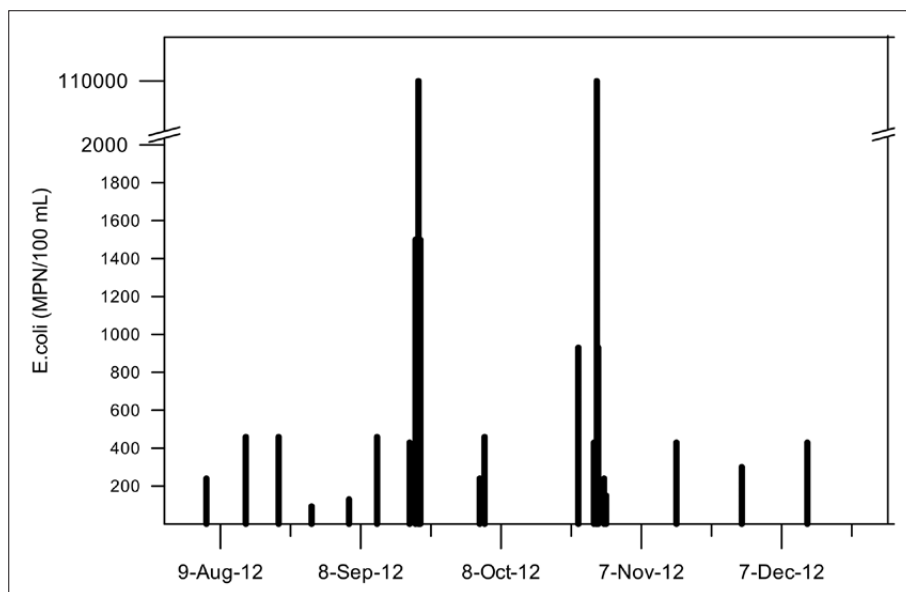


Fig. 7: Detected *Escherichia coli* (MPN/100 mL) in the drinking water spring 18.

cause contamination. Tracer results clearly provided that contamination from spring 20 could easily load to spring 18 in a short time and then could be polluted into the karst aquifer. A fence constructed around the pumping station at spring 18, therefore, is insufficient to protect this drinking water source. To protect drinking water

sources, groundwater source protection zones and flexible water quality monitoring with regard to the typical characteristic of the Dong Giao karst aquifer should be essential acts. Groundwater vulnerability, hazard and risk maps are recommended to apply in the Tam Diep area to minimize the risk to public health.

CONCLUSIONS

The interpretation of physical-chemical parameters of all main karst springs and domestic water wells has revealed the hydrogeochemical characterization and factors governing water chemistry in the vicinity of Tam Diep city. The groundwater hydrochemical facies are classified as calcium magnesium bicarbonate (Ca-Mg-HCO₃) type and calcium bicarbonate (Ca-HCO₃) type suggest that the dissolution of carbonate rocks of Dong Giao formation is controlling groundwater chemistry. The well-fitting dissolution line (1:2) of total calcium and magnesium to alkalinity further indicates the weathering process of carbonate rocks within the aquifer. The water-rock interaction and the various lithologies of the Dong Giao carbonate rocks are proved by groundwater Ca/Mg ratios.

Chemical parameters at karst springs and domestic wells are highly variable, but their values are lower than recommended limits of WHO and Vietnamese standards for drinking water. The hydrochemical water quality is good for drinking. The calculated SAR values

also indicate that the groundwater has excellent to good quality for irrigation purposes. However, based on total hardness values, most of the groundwater samples are hard and very hard water types (TH > 150 mg/L CaCO₃) which are considered undesirable levels for drinking water. Microbial investigation at the important drinking water spring 18 and other main karst springs shows that all samples contain high bacteria (*E.coli*) concentrations, and thus microbial groundwater quality is unsafe for drinking purposes. Untreated domestic wastewater, city sewage, rapid urbanization and human activities have caused a negative impact on the karst groundwater quality in the area.

The results of this work provide valuable information for groundwater exploration, protection and management of water resources in the area. It is recommended that groundwater vulnerability mapping, hazard and risk maps and appropriate water treatment should be considered to insure safe drinking water in the Tam Diep area.

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REFERENCES

- Barberá, J.A. & B. Andreo, 2012: Functioning of a karst aquifer from Spain under highly variable climate conditions, deduced from hydrochemical records.- *Environ Earth Sci*, 65, 2337–2349.
- Drew, D. & H. Hötzl (eds), 1999: *Karst Hydrogeology and Human Activities. Impacts, Consequences and Implications*.- International Contributions to hydrogeology, 20. Balkema, pp 322, Rotterdam.
- Ford, D.C. & P. Williams, 2007: *Karst hydrogeology and geomorphology*.- John Wiley & Sons, pp. 562, Chichester.
- Gibbs, R., 1970: Mechanisms controlling world water chemistry.- *Science*, 170, 1088–1090.
- Goldscheider, N., 2012: A holistic approach to groundwater protection and ecosystem services in karst terrains.- *Aqua Mundi – Am*, 06046, 117–124.
- Hunkeler, D & J. Mudry, 2007: Hydrochemical methods. – In Goldscheider, N & D. David (eds) *Methods in Karst Hydrogeology*.- Taylor & Francis, pp. 93–121.
- Huu, N.D. & D.T Huong, 2012: Outcrop of dolomite in lower part of Dong Giao Formation, NW Vietnam.- *Vietnam Journal of Geology*, 329, 46–55 (in Vietnamese).
- Krishna Kumar, S.N., Chandrasekar. P., Seralathan. P.S., Godson & N.S. Magesh, 2012: Hydrogeochemical study of shallow carbonate aquifers, Rameswaram Island India.- *Environ Monit Assess*, 184:4127–4138.
- MONRE, 2008: National technical regulation on underground water quality.- Ministry of Environment and Natural Resources (in Vietnamese).
- Mudarra, M. & B. Andreo, 2010: Hydrogeological functioning of karst aquifer deduced from hydrochemical components and natural organic tracers present in springs waters. The case of Yedra spring (southern Spain).- *Acta Carsologica*, 39(2), 261–270.
- Nguyet, V.T.M. & N. Goldscheider, 2006: Tracer tests, hydrochemical and microbiological investigations as a basis for groundwater protection in a remote tropical mountainous karst area, Vietnam.- *Hydrogeology Journal*, 14(7), 1147–1159.
- Parkhurst, D. & C.A.J. Appelo, 2011: PHREEQC version 3–A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.- Water Resources Div. Denver, CO.
- Pasquarell, G.C & D.G. Boyer, 1995: Agricultural impacts on bacterial water quality in karst groundwater.- *J Environ Qual*, 24 (5), 959–969.
- Pronk, M., Goldscheider, N & J. Zopfi, 2006: Dynamics and interaction of organic carbon, turbidity and bacteria in a karst aquifer system.- *Hydrogeology Journal*, 14, 473–484.
- Pu, J., Yuan, D.X., Xiao, Q & H. Zhao, 2015: Hydrogeochemical characteristics in karst subterranean streams: a case history from Chongqing, China.- *Carbonates Evaporites*, 30, 307–319.
- Sánchez, D., Barberá, J.A., Mudarra, M & B. Andreo, 2015: Hydrogeochemical tool applied to the study of carbonate aquifers: examples from some karst systems of Southern Spain.- *Environ Earth Sci*, 74, 199–215.
- Thin, T.T., Sang, N.V., Ngu, L.V & T.H. Luan, 1982: *Groundwater investigation in Tam Diep area*.- Division for groundwater investigation for the north of Vietnam – General Department of Geology of Vietnam, pp. 133. (in Vietnamese).
- US Environmental Protection Agency, 1986: Quality criteria for water 1986.- EPA 440/5-86-001. Washington, DC 20460.
- USSL, 1954: Diagnosis and improvement of salinity and alkaline soil.- USDA Hand Book no.60, Washington.
- Wilcox, LV, 1955: Classification and use of irrigation waters.- USDA Circ. 969, Washington, DC.
- White, W.B., 1988: *Geomorphology and hydrology of karst terrains*.- Oxford University Press, pp.464, New York.
- White, W.B., 2010: Springwater geochemistry.- In Kresic, N & Z. Stevanovic (eds) *Groundwater Hydrology of Springs – Engineering, Theory, Management and Sustainability*.- Elsevier, pp. 231–268.
- Zwahlen, F.(ed), 2004: *Vulnerability and Risk Mapping for the Protection of Carbonate (Karst) Aquifer*.- Final report COST Action 620, EUR 20912. European Commission, Directorate-General for Research, pp.297, Luxemburg.